(12) **Patent:** (11) **CA 472170**

(54) METHODS OF PRODUCING LOW-GLARE COATINGS

(54) METHODES DE PRODUCTION D'ENDUITS PEU EBLOUISSANTS

ABSTRACT:

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to methods of producing low-glare surfaces on glass or the like, and has for its principal object the provision of an improved low-glare surfacing process by which the object to be treated is immersed in a solution whereby predetermined elements of the treated surfaces are removed or leached out leaving a skeletonized film or surface of such thickness as to be low-reflective to light of a selected wave length.

Skeletonized silica films on glass have been produced heretofore by the use of hydrofluoric acid vapor and by the vapor of hydrofluosilicic acid. In this way, a large variety of glasses have been treated so as to reduce or eliminate reflection from the treated surface. It has been recognized for some time, however, that a solution method of treatment would have certain advantages not inherent in the acid vapor method of treatment. For example, the vapor method of coating usually produces a coating on only one surface while a solution method is readily utilized to coat all surfaces of the object. The solution method also involves no temperature differential between the solution and the object treated and is otherwise more readily practiced than some of the vapor processes heretofore used.

The invention will be better understood from the following description considered in connection with the accompanying drawings and its scope is indicated by the appended claims.

Referring to the drawings:

Figure 1 is a curve showing the variation in the amount of glass dissolved with the time that the glass is maintained in an 18% fluosilicic acid solution at 45° C.,

Figure 2 is a curve showing the variation in the amount of silica dissolved with the time that the fused silica is in the acid at 45° C.,

Figure 3 is a curve showing the effect of acid concentration on the metal fluosilicate concentration in a working solution,

Figure 4 illustrates the effect of acid concentration on the time required to form a non-reflective coating of predetermined thickness, and

Figure 5 is a pair of curves showing certain relations between temperature and the time required to produce a non-reflective coating.

The solution method of the present invention involves in general, a treating solution made by digesting or dissolving glass of the type to be treated in fluosilicic acid or the equivalent until the solution reaches a point such that it selectively removes the non-film forming constituents of the treated glass surface and produces a skeletonized film or coating of the remaining constituents of the glass surface.

As applied to silica glasses, this means that silica glass, or its equivalent, is dissolved in fluosilicic acid ($H_2\ Si\ F_6$), that the non-siliceous constituents are differentially leached out or dissolved from the treated surface and that the resulting coating is skeletonized and altogether or largely constituted of silica.

Thus it is found, for example, that a solution suitable for producing a low index film on window glass and the like is made from 600 c.c. of 16% fluosilicic acid ($H_2\ Si\ F_6$) in which is maintained for fifteen hours at a temperature of 45° C. a piece of window glass having a total surface area of about three square feet.

The pieces of glass in the solution of fluosilicic acid plus glass are periodically examined and their characteristic

appearance indicates the progress of formation of the final treating solution. These steps are as follows: Soon after placing the glass in solution the pieces are observed to have been strongly eaten away by the acid, the surface still having a polished appearance. At this point, any glass protruding into the vapor will have a low reflection film on it. As the digestion of the glass continues the attack on the glass in solution becomes less and less film is formed in the vapor. As this condition is reached (after several hours), it is observed that a low reflection film is formed on the glass at the meniscus and in any "trapped volumes" (regions where two pieces of glass almost touch thus including a small volume of acid in contact with a large area of glass). These "trapped volumes" are the first regions to reach the correct conditions for producing low reflection films. When the time of digestion is further continued, the exposed surfaces of the glass begin to show interference colors but the reflection is still not low since the non-siliceous material is not yet completely removed and the film has an index of refraction probably around 1.4.

After a further period of digestion, the glass surface becomes more highly colored with corresponding indications of low refractive index in the surface film.

At this point, the undissolved glass is removed and the solution is ready for producing a low-reflecting film on a new piece of glass which is immersed in the solution at this point. Such a solution produces a film of low reflection to green light in about one-half hour. This film is on both sides of the glass and is satisfactory with respect to hardness and other mechanical properties.

The preparation of a treating solution as described is

typical of the method in which glass is digested in an acid in order to bring about changes in the solution which will eventually produce a solution capable of selectively removing the non-siliceous parts of the glass. In general, tests performed on the glass at various times after mixing will give the results described above.

The method of preparing a treating solution may also consist of digesting glass in a mineral acid to which has been added a small quantity of hydrofluoric acid. The digestion of the glass surface goes through the various stages described above until satisfactory low index films are obtained. Low reflection films have been obtained using acids such as H_2SO_4, HCl, HNO_3, H_3PO_4, and also with salts of these acids. In each case it is essential that some HF be added. These acids even when hot will not produce low index films of low reflection on crown or lime glasses.

The mechanism of formation of the low index skeletonized film seems to depend on some action by the HF. This acid seems to remove enough silica so that the other mineral acid present is able to remove the non-siliceous component which, without the presence of HF, it would not be able to do to any great extent.

The digestion of the glass in the acid solutions appears to be merely a method of altering pH and fluoride ion concentration and in addition the amount of salts in solution. These two quantities will not be the same for treating different glasses but a solution being prepared by glass digestion will, after a certain length of time treat one type of glass whereas further digestion may be necessary to reach the point at which another type of glass can be treated. Thus, for example, a solution of lead glass digested in fluosilicic acid reaches at some later time a condition in which it will satisfactorily treat lime glass.

The necessity for dissolving in the solution glass of the type which is to be coated may be avoided if the solution is made to have the desired constituents by dissolving the required ingredients in it. Thus, a solution suitable for treating silica glass is made by dissolving in fluosilicic acid, silica and sodium and calcium fluosilicates.

It is important that the pH or hydrogen ion concentration be just right and that the solution may be at the same time almost saturated with the dissolved salts of the alkali metals in the treated glass. Some silica is also present in the solution. This keeps the HF concentration very low, reducing the F ion concentration to a point where hardly any silica is removed from the treated surface. Otherwise stated, there is a differential leaching out of the constituents of the treated surface leaving a skeletonized film consisting largely of silica.

Fig. 1 shows the variation in the amount of glass dissolved with the time that the glass is in a 16% fluosilicic acid solution at 45° C. The velocity of a liquid-solid interface reaction can be expressed in the following form.

$$\frac{dc}{dt} = k' (a-c)^n$$

where

a = the solubility of the solid in the liquid

c = the concentration of the solute in the solution at time, t

n = the order of the reaction

By graphical differentation of the curve of concentration of dissolved glass versus time of immersion and plotting log $\left(\frac{dc}{dt}\right)$ against log (a-c), the process of solution has been found to be

best described as a second order reaction, particularly if the solubility of the glass in the acid is taken as 24 mg./ml. Actually, the order of the reaction appears to be changing with time, especially when the solution approaches saturation. This indicates that the actual mechanism of solution is changing with the amount of dissolved glass. After 15 hours the mechanism has sufficiently changed so that silica is no longer being dissolved as rapidly as the metal oxides, and a silica film results. At this stage, the 16 % fluosilicic acid solution contains approximately 20 mg. of glass per ml. of solution. From chemical analysis of the actual glass dissolved about 63 % (12.5 mg.) is silica and about 37% (7.5 mg.) are metal oxides.

The structure of glass is recognized as consisting of a rigid silica network into which is interdispersed the metal oxides. Because the glass is uniformly removed during the process of solution, it must be that the silica is attacked more rapidly than the metal oxides. To check this, the rate of solution of fused silica in 16% fluosilicic acid was investigated. Fig. 2 shows the variation in the amount of silica dissolved with the time that the fused silica is in the acid at 45° C. Although the rate of solution of the silica is apparently independent over several orders of magnitude of the concentration of dissolved silica, when the concentration of dissolved silica becomes about 40% of the saturation value the curve takes a form similar to Fig. 1. By graphical differentation of the curve of concentration of dissolved silica versus time of immersion and plotting log $\frac{dc}{dt}$ against log (a-c), the process of solution is again found to be best described as a second order reaction, particularly if the solubility of the silica is taken as 11 mg./ml. It may be concluded that, although the actual velocity of solution is about

a 100 times greater for glass than for fused silica (correcting the curves to the same surface area per unit volume of solution), the actual mechanism of solution is quite similar, at least up to the point where the film starts to form in the case of the glass. After the 16% fluosilicic acid solution has dissolved about 8mg. of silica p er ml. of solution, the rate of attack becomes almost neglibible. If glass is now immersed in this solution, the glass is removed uniformly and no film results. In other words, the presence of metal oxides from the glass appears to increase the capacity of the solution to dissolve silica. This would be expected since the metal oxides (as the fluorides) react with the dissolved silica (in the form of silicon tetrafluoride) to form metal fluosilicates.

From the previous results, it seems probable that for each concentration of acid and for each glass composition, a solution must have a fairly specific concentration of metal oxides and silica, most likely combined as the fluosilicates. In order to investigate the effect of acid concentration on the metal fluosilicate concentration for a working solution, a series of working solutions were made up under identical conditions by immersing at 45° C. a square foot of Libbey Owens Ford window glass in 400 ml. of each solution. After the solutions had been shown to produce low-index films on glass, each was gravimetically analyzed, The results were checked by volumetric analysis, and both results are shown in Fig. 3. Over the range of 4% to 16% by weight fluosilicate acid, the fluosilicate concentration is a linear function of the acid concentration. Because the metal fluosilicates are almost completely ionized, neglecting the contribution from the slight secondary ionization of fluosilicic acid, the $SiF_6^{=}$ concentration is equal to the metal fluosilicate

concentration. If the equilibrium constant for the following reaction is considered:

$$H_2SiF_6 \rightleftharpoons 2H^+ + SiF_6^=$$

$$K_1 = \frac{C_{H^+}^2 \times C_{SiF_6^=}}{C_{H_2SiF_6}}$$

it is apparent that the hydrogen ion concentration must be constant for a working solution because the $SiF_6^=$ concentration is a linear function of the H_2SiF_6 concentration. In other words, the acid solution is strongly buffered by the salt. To check the result, attempts were made to determine the pH of working solutions of various acid concentrations. Because the pH of the solution is quite low, the foreign ion concentration is quite high, and the solution slowly attacks glass, the measurement of pH is not easy. The most satisfactory results were obtained with the glass electrode. The pH appeared constant at about 1.2 for solutions varying in acid concentration from 4% to 28% H_2SiF_6, although the pH reading drifted as much as half a pH unit because of attack on the electrode. Having the pH, the $SiF_6^=$ ion concentration, and the H_2SiF_6 concentration it is a simple matter to calculate the equilibrium constant of the above reaction. Because the contribution of $SiF_6^=$ from the secondary ionization of H_2SiF_6 is very small and because the primary ionization of H_2SiF_6 results in only $HSiF_6^-$, the $SiF_6^=$ concentration is considered as equal to the concentration of $MSiF_6$ as these salts are practically completely ionized. On this basis K_1 has a value of 3.2×10^{-4} moles ^{2}/liter^2, at least in a working solution. During the determination of dissolved fluosilicates as a function of acid concentration for a treating solution, the time required to form

...er wave film was also determined as a function of acid concentration. From the results shown in Fig. 4, it is apparent that the process of film formation is a second order reaction. This confirms the less direct measurements made on the fluosilicic acid vapor process.

In a solution which produces a low-index silica film on glass, there are many molecular species present although, because of equilibrium considerations, the actual concentrations may be very small. From a study of various equilibrium constants and from the concentrations of known constituents, at least a qualitative idea may be obtained as to the concentrations of the other constituents. The following reactions and their equilibrium constants give the relationships between the most important molecular species in the system.

Reaction 1

$$H_2SiF_6 \rightleftarrows H^+ + HSiF_6^- \rightleftarrows H^+ + SiF_6^{=}$$

$$K_1 = \frac{C^2_{H^+} \times C_{SiF_6^=}}{C_{H_2SiF_6}} = 3.2 \times 10^{-4} \text{ at } 45^\circ \text{ C.}$$

Reaction 2

$$SiF_6^{=} \rightleftarrows 2F^- + SiF_4$$

$$K_2 = \frac{C_{F^-}^{\,2} \times C_{SiF_4}}{C_{SiF_6^=}} = 10^{-6} \text{ at } 20^\circ \text{ C.}$$

Reaction 3

$$H_2SiF_6 \rightleftarrows 2H^+ + 2F^- + SiF_4$$

$$K_3 = \frac{C_{H^+}^{\,2} \times C_{F^-}^{\,2} \times C_{SiF_4}}{C_{H_2SiF_6}} = K_1 K_2 = 3 \times 10^{-10} \text{ at } 30^\circ \text{ C.}$$

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Reaction 4

$$H_2SiF_6 \rightleftharpoons 2HF + SiF_4$$

$$K_4 = \frac{C_{HF}^{2} \times C_{SiF_4}}{C_{H_2SiF_6}} = 4 \times 10^{-5} \text{ at } 25^\circ \text{ C.}$$

Reaction 5

$$HF \rightleftharpoons H^+ + F^-$$

$$K_5 = \frac{C_{H^+} \times C_{F^-}}{C_{HF}} = \sqrt{K_3/K_4} = 3 \times 10^{-3} \text{ about } 27^\circ \text{ C.}$$

The equilibrium constant for reaction 5, derived from the above constants agrees, within its variation with concentration, with the value determined from conductivity measurement. On the basis of the above equilibrium constants, it may be concluded that the H F concentration is very low and the F^- concentration is extremely low. This probably explains why the solution attacks silica so slowly, if at all. It has been confirmed that the H F concentration is very low since the time required to treat glass with the vapor of a 16% fluosilicic acid solution which treats glass in solution is long. It is known from the work with H F vapor that this corresponds to very little free H F in solution. Chemical analysis of the vapor indicated that the vapor of this solution has the same H F concentration as that of a 0.05% hydrofluoric acid solution. Although most of the dissolved silica exists in solution as SiF_4 and $SiF_6^{=}$, even pure H_2SiF_6 solutions may contain at least 0.003 mols per liter of silicic acid as such, and a working solution, saturated with silica undoubtedly contains more. In general, the identity of the cation associated with the fluosilicate ion seems unimportant. Only the number of such ions is important to buffer the solution at constant pH. For example, solutions made up by dissolving lead glass in 16% fluosilicic acid

have been found to treat window glass satisfactorily. Also, solutions made up by dissolving various ratios of CaO to Na_2O plus SiO_2 have been found to treat window glass equally well.

During earlier work on the solution method of producing low-index silica films on glass, considerable difficulty was encountered in obtaining consistent and reproducible results because of the limited tolerances on certain variables. If a 16% fluosilicic acid working solution loses 10% of its volume by evaporation, the solution ceases to work, and treats only at the meniscus and in trapped areas. If this solution is now diluted almost back to the original volume, the solution again works satisfactorily. This shows that little is lost on evaporation except H_2O. On the other hand, if a 16% fluosilicic acid working solution is diluted to twice its volume, the solution ceases to produce a low-index film, and apparently does not attack the glass at all. If 0.2 ml. of 30% H_2SiF_6 is added to each 100 ml. of diluted solution, the solution again produces a low-index film, of course, in a longer period than the original solution. The addition of excess of C.P. silica has been found to have an adverse effect on the working properties of the solution, notwithstanding the fact that a working solution usually contains pieces of skeletonized film floating around in it. One of the important properties of a working solution is the pH. This may be adjusted by the addition of concentrated H_2SiF_6 and concentrated NaOH. The addition of the acid results in an increased amount of acid per unit amount of salt whereas the addition of alkali results in increased amount of salt. In other words, the critical feature for a working solution is the tolerance on points on the curve shown in Fig. 3.

It is worth noting that a symptom of excess fluosilicate is a high index film in the solution, while the symptom of excess acid is a low index film at the meniscus and in the vapor with

considerable uniform glass removal in the solution. To determine whether a solution will actually treat glass, without actually trying to make a film, is a difficult problem, particularly in regard to satisfying the pH requirement. On the basis of the difficulty encountered in merely measuring the pH approximately as a function of concentration of acid, it is obvious that no ordinary pH meter will distinguish between a solution that just treats glass and one that does not. The most encouraging procedure, to date, to distinguish between working and non-working solutions, without actually trying to make a film, is based on the volumetric method of determining the hydrofluoric and fluosilicic acid in a solution. Here, however, the solution is not a mixture of these acids, but consists of metal fluosilicate and fluosilicic acid. The reactions occurring at 0^{o} C. with methyl orange indicator are the following:

$$H_2SiF_6 + 2\ NaOH \rightarrow Na_2SiF_6 + 2\ H_2O$$

$$MSiF_6 + NaOH \rightarrow \text{no reaction}$$

At 25^{o} C. with phenolphthalin indicator, the reactions are the following:

$$H_2SiF_6 + 6\ NaOH \rightarrow 6\ NaF + SiO_2 + 4\ H_2O$$

$$MSiF_6 + 4\ NaOH \rightarrow 4\ NaF + MF_2 + SiO_2 + 2\ H_2O$$

If there were no metal fluosilicate present and no free HF, the ratio of the alkali used with the room temperature titration to the alkali used with the low temperature titration would be 3.00. For a working 16% fluosilicic acid solution (containing 1.25 moles/liter of H_2SiF_6 and 0.10 moles/liter of $MSiF_6$), the ratio is experimentally found to be 3.25. The exact value of this ratio depends on what the observer considers as the end point in the two titrations. It has been found possible to distinguish between a non-working solution and a solution of the same acid concentration

..d known to be working if the two titrations for each solution are carried out at the same time to identical end points and if the titrations are made to the standard accuracy of one part in a thousand. A series of experiments were carried out in which the acid content was varied in a working solution. The total tolerance on the acid concentration was found to be 0.015 equivalents per liter of a solution containing 7.5 equivalents per liter. This amounts to two parts per thousand on acid tolerance for a 16 per-cent solution working at 45° C. Incidentally, if the amount of the acid varies by as much as 0.2 equivalents per liter, the solution can be adjusted to a working condition by adding approximately the equivalent amount of alkali or acid by which the acid concentration deviates from that of the working solution.

The fluosilicic acid vapor process is not suitable for use at other than room temperature. This is not the case for a solution process. Most of the work on the fluosilicic acid solution method has been done at 45° C. as a matter of convenience of experiment and because of the relatively short time required to make a quarter-wave film. For example, above 50° C. ceresin wax containers melt and above 55° C. the Harvel insulating varnish used shows evidence of attack in the vapor process by 16% fluosilicic acid. Therefore, in investigating the process as a function of temperature, a platinum distillation flask of 100 ml. capacity was used. A 16% solution prepared at 45° C. was found to produce low-index films between 35° C. and 55° C. Below 35° C. the solution failed to attack the glass at all, whereas above 55° C. the solution removed glass uniformly and produced only a narrow film at the meniscus.

The temperature dependence of the time required to make a quarter-wave film is shown by curve 1 in Figure 5. The heat of

activation of the process of film formation can be calculated from this curve and is found to be the same as the heat of activation for film formation by the vapor process.

$$\Delta H = R \frac{d(\ln t)}{d(1/T)} = 15.1 \text{ k'cal.}$$

One way of preparing a solution to treat glass above 55° C. is to add alkali solution to the 16 percent fluosilicic acid working solution prepared at 45° C. The following table gives the volume of 10 NNaOH required to make 100 ml. of the 45° C. solution work at the specified temperature. The time to produce a quarter-wave film is also included. In most cases the solution was tested by making a film within an hour after the alkali addition, and the resulting films were not always completely uniform.

Temperature	Vol.10 NNaOH	Time
60° C.	.2 ml.	13 min.
65° C.	.4 ml.	10.5 min.
70° C.	.8 ml.	8.5 min.
75° C.	1.2 ml.	6.5 min.
80° C.	1.6 ml.	5 min.
85° C.	2.6 ml.	4 min.
90° C.	5.2 ml.	3 min.
95° C.	7.0 ml.	2.5 min.
100° C.	8.5 ml.	2 min.

The time to produce a quarter-wave film is also shown by curve 2 of Figure 5. The slope of this curve is not a measure of the heat of activation because the acid concentration is being decreased with increasing temperature since NaOH has been added at each experimental point. It is interesting to note that if curve 1 is continued to 100° C. the time of treatment would be one minute. At 100° C. curve 2 indicates two minutes and it can be calculated from the amount of alkali added that about half the fluosilicic

acid has been changed to fluosilicate at this temperature. This agrees with the previous results shown in Figure 4 that the time of treatment varies inversely with acid concentration. Also, it can be concluded that the heat of activation and therefore the mechanism are independent of temperature. It is probable that at least two factors adjust the solution to a treating condition on the addition of alkali at each temperature. First, sufficient fluosilicate must be formed at each temperature to almost saturate the solution. Sodium fluosilicate is twice as soluble in water at 100° C. as at 45° C., and although fluosilicates are more soluble in fluosilicic acid than in water, the temperature dependence of the solubility is similar. The addition of the tabulated amount of alkali more than satisfied the solubility requirement since sufficient fluosilicate is formed to result in a precipitate. In other words, the acid concentration apparently must be decreased to a new value at each temperature, although the solution may already be saturated with fluosilicates. A possible explanation of this effect is that the activity of the fluoride increases with temperature and because no silica is being added to keep the fluoride ion activity down, it is necessary to decrease the total acid concentration with alkali.

The actual process of silica film formation on the glass surface is a differential rate process in a strongly buffered solution. When fluosilicic acid attacks glass, the silica network is attacked by the following second order reaction:

$$2\ H_2SiF_6 + SiO_2 \longrightarrow 3\ SiF_4 + 2\ H_2O$$

Eventually sufficient silicon tetrafluoride and metal fluosilicates are formed, so that the above reaction takes place very slowly. Then the metal oxides are selectively removed, and a skeletonized silica film results. The process continues because the dissolved

metal oxides unite with silicon tetrafluoride, so that the silica may be slightly attacked in order to get at the metal oxides interdispersed in the rigid silica network. Liquid-solution interface reactions are in general divided into reactions that are limited by the diffusion of the reactants to the interface, by the diffusion of reaction products from the interface, and by the actual reaction at the interface. Because the limiting reaction is a second order reaction (diffusion processes are unimolecular) and because stirring apparently has no effect on the rate of film formation, it seems that the actual reaction at the interface is the limiting process. Also, the rate of increase of film thickness appears to be independent of the thickness of the film at least up to several wavelengths thick. This indicates that it is not diffusion through the film that limits the process.

During the treatment, the glass is supported at any convenient point in the liquid but not touching the bottom of the container or the surface of the liquid. A satisfactory means of support is a cradle or framework touching only the edges of the treated glass.

The temperature of the solution during treatment of the glass is not critical. Good non-reflective films have been made at 100° C. in one or two minutes. Evaporation of the solution at this temperature and the difficulty of finding sufficiently rugged containers, however, make it desirable to operate at a lower temperature of the order of 65° C., for example.

Having regard to the foregoing disclosure, the patent of which this specification forms part confers, subject to the conditions prescribed in the Patent Act, 1935, the exclusive right, privilege and liberty of making, constructing, using and vending to others to be used, the invention as defined in claims submitted by the patentees as follows:

1. The method of forming on the surface of a slica glass object a low-reflectance skeletal film consisting essentially of silica and having a thickness of the order of an odd number of quarter wave lengths of light, said method comprising dissolving in a solution including fluosilicic acid about 20 mg. per ml. of a soda-lime-silica glass, said dissolved glass comprising about 63 per cent silica and about 37 per cent metallic oxides and immersing said object in said solution until said low-reflectance film is formed.

2. The method of claim 1 in which there is also present in said solution a mineral acid.

3. The method of forming on the surface of a silica glass object a low-reflectance skeletal film consisting essentially of silica and having a thickness of the order of an odd number of quarter wave lengths of light, said method comprising dissolving in a solution including a mineral acid and a minor amount of hydrofluoric acid about 20 mg. per ml. of a soda-lime-silica glass, said dissolved glass comprising about 63 per cent silica and about 37 per cent metallic oxides and immersing said object in said solution until said low-reflectance film is formed.

4. The method of forming on the surface of a silica glass object a low-reflectance skeletal film consisting essentially of silica and having a desired thickness of the order of an odd number of quarter wave lengths of light, said method comprising immersing partially in a solution including fluosilicic acid a piece of a silica-containing glass, continuing said immersion until there is formed on a surface of said glass protruding above said solution a film having said desired thickness, removing the glass thus treated, immersing in said solution a fresh piece of a silica-glass, and continuing said last immersion until said fresh piece of glass has acquired a low reflectance surface film having said desired thickness.

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5. A method according to claim 4 in which said last mentioned glass is a soda, lime glass.

6. A method according to claim 4 in which said solution also contains a mineral acid.

7. In the production of a low-reflectance skeletal film consisting essentially of silica and having a desired thickness of the order of an odd number of quarter wavelengths of light, said method comprising immersing partially in a solution comprising a mineral acid and a minor proportion of hydrofluoric acid a piece of a silica-containing glass, continuing said immersion until there is formed on a surface of said glass protruding above said solution a film having said desired thickness, removing the glass thus treated, immersing in said solution a fresh piece of a silica-containing glass and continuing said immersion until said fresh piece of glass has acquired a low reflectance film having said desired thickness.

(A)

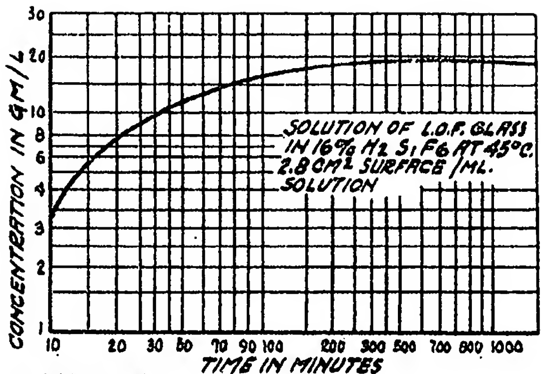


Fig.1.

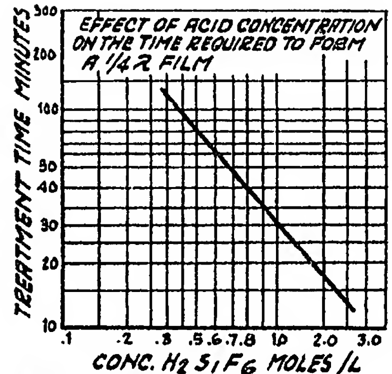


Fig.4.

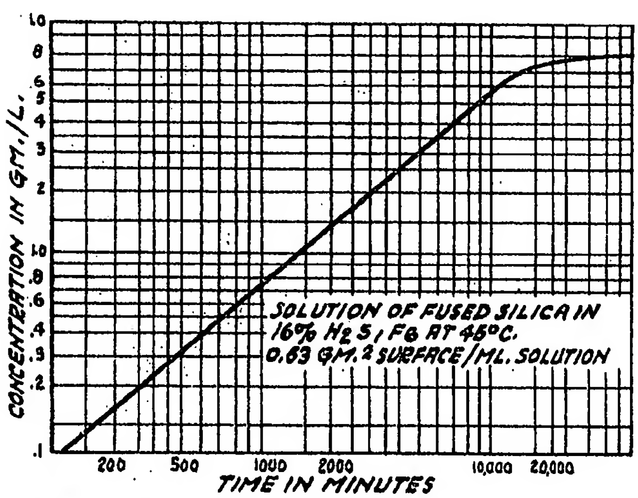


Fig.2.

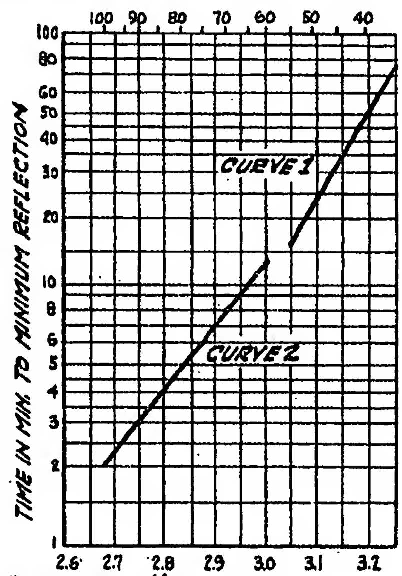
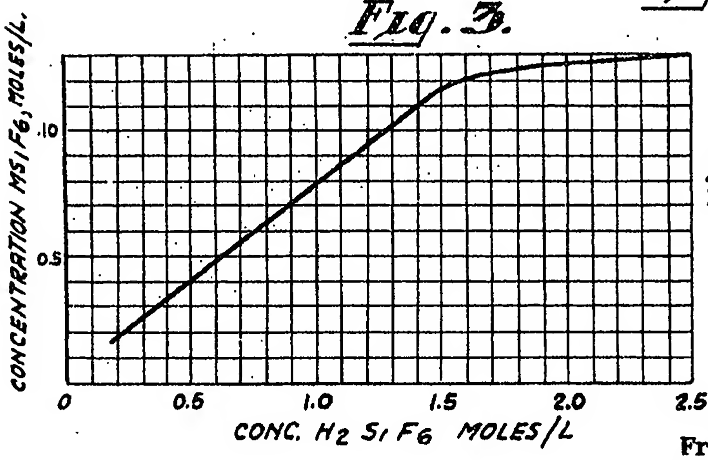


Fig.5. $1/T_{ABS} \times 10^3$

Fig.3.



DISSOLVED FLUOSILICATE AS A FUNCTION OF ACID CONCENTRATION FOR A WORKING SOLUTION AT 45°C

Frederi k Hermes Nicoll
Ferd Elton Williams
INVENTOR S

Certified to be the drawings referred to in the specificati n hereunto annexed.

Montreal, Que., Nov. 26th 1945.

ATTORNEY